

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2003-059490

(43)Date of publication of application : 28.02.2003

(51)Int.Cl.

H01M 4/58

H01M 10/40

(21)Application number : 2001-247816

(71)Applicant : TANAKA CHEMICAL CORP

(22)Date of filing : 17.08.2001

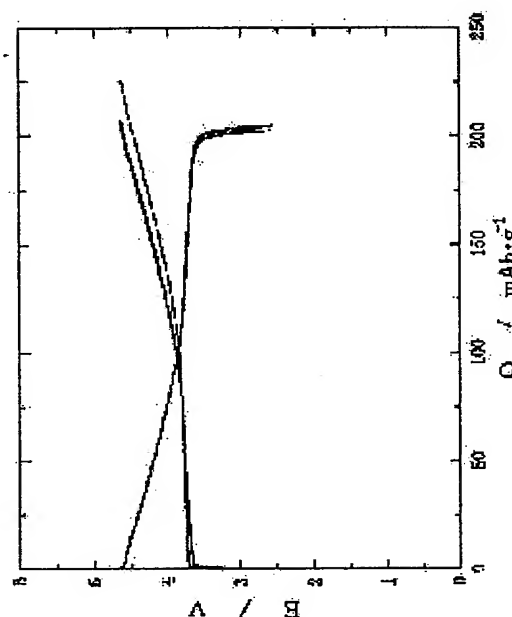
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(54) POSITIVE ACTIVE MATERIAL FOR NONAQUEOUS ELECTROLYTE SECONDARY BATTERY AND ITS MANUFACTURING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a lithium nickel cobalt manganese composite oxide with high characteristics and useful as a positive active material for a lithium ion secondary battery, its manufacturing method, and the lithium ion secondary battery using this composite oxide.

SOLUTION: The lithium nickel cobalt manganese composite oxide is represented by the composition formula of $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ in which the actual atomic ratio of nickel, cobalt, and manganese is 1:1:1, has high crystalline layered structure of a rhombohedral system, and the length of a C axis belonging as a hexagonal system is 14.15 Å or more.



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CLAIMS

[Claim(s)]

[Claim 1]Positive active material for nonaqueous electrolyte secondary batteries which consists of a crystal grain child of an oxide of high crystallinity which contains a nickel element, a cobalt element, and a manganese element of the ratio substantially.

[Claim 2]The positive active material for nonaqueous electrolyte secondary batteries according to claim 1, wherein said oxide contains lithium elements.

[Claim 3]Claim 1, wherein an error of a ratio of a nickel element, a cobalt element, and a manganese element is less than ten atom %, or positive active material for nonaqueous electrolyte secondary batteries given in either of 2.

[Claim 4]The positive active material for nonaqueous electrolyte secondary batteries according to any one of claims 1 to 3, wherein lithium elements, a nickel element and a cobalt element which are contained in said oxide, and a manganese element fill $0.97 \leq \text{Li}/(\text{nickel}+\text{Co}+\text{Mn}) \leq 1.03$.

[Claim 5]A manufacturing method of the lithium nickel cobalt manganese multiple oxide according to any one of claims 1 to 4 characterized by comprising the following.

An atomic ratio of nickel, cobalt, and manganese reacts to an alkali solution a mixed water solution of nickel salt, cobalt salt, and manganese salt which are 1:1:1 substantially under an inert gas atmosphere under existence of a complexing agent in solution of pH 9-13, The process 1 from which it acts as Mr. [coprecipitation] and an atomic ratio of nickel, cobalt, and manganese obtains nickel cobalt manganese compound hydroxide and/or a nickel cobalt manganese multiple oxide which are 1:1:1 substantially.

The process 2 of calcinating a mixture of said hydroxide and/or an oxide, and a lithium compound above 700 ** so that an atomic ratio of the sum total of nickel, cobalt, and manganese and an atomic ratio of lithium may be substantially set to 1:1.

[Claim 6]A rechargeable lithium-ion battery containing the lithium nickel cobalt manganese multiple oxide according to any one of claims 1 to 4 as a positive-electrode-active-material ingredient.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to a lithium nickel cobalt manganese multiple oxide useful as positive active material for rechargeable lithium-ion batteries which has the outstanding characteristic and a manufacturing method for the same, and the rechargeable lithium-ion battery using it further.

[0002]

[Description of the Prior Art]In recent years, the request on the cell of small size, a light weight, and high energy density has become strong with the spread of cordless and portable AV equipment, personal computers, etc. also about the cell which are those power supplies for a drive. Since it is a cell which has high energy density, especially the lithium secondary battery is expected as a next-generation prime cell. Although LiCoO_2 which has the high tension of 4V as positive active material is used, since Co is expensive, the price of most lithium secondary batteries marketed now is high. What has the performance which was cheap from this, did not spoil the performance which was excellent in LiCoO_2 , or was more excellent is demanded.

[0003]

[Means for Solving the Problem]By this invention person's inquiring wholeheartedly that it should search for a substance which replaces LiCoO_2 which fills this request, and using a manufacturing method explained below, nickel $_{1/3}$ Co $_{1/3}$ Mn $_{1/3}$ Li $_{1/3}$ O $_2$ whose atomic ratio of nickel, cobalt, and manganese is 1:1:1 substantially as 4 Class V positive active material — what has a presentation, It found out having the outstanding characteristic of versatility which applying to a rechargeable lithium-ion battery is expected. It finds out that a rechargeable lithium-ion battery which has the outstanding characteristic using a lithium manganese nickel multiple oxide concerning this this invention can be obtained, and came to complete this invention.

[0004]That is, positive active material for nonaqueous electrolyte secondary batteries concerning this invention is positive active material for nonaqueous electrolyte secondary batteries which consists of a crystal grain child of an oxide who has the structure of high crystallinity which contains a nickel element, a cobalt element, and a manganese element of the ratio substantially. As for positive active material for nonaqueous electrolyte secondary batteries concerning this invention, said oxide contains lithium elements. Positive active material for nonaqueous electrolyte secondary batteries concerning this invention is characterized by an error of a ratio of a nickel element, a cobalt element, and a manganese element being less than ten atom %. Lithium elements, a nickel element and a cobalt element in which positive active material for nonaqueous electrolyte secondary batteries concerning this invention is contained in said oxide, and a manganese element fill $0.97 \leq \text{Li}/(\text{nickel}+\text{Co}+\text{Mn}) \leq 1.03$. Here as a crystal structure feature of positive active material for nonaqueous electrolyte secondary batteries concerning this invention, It has the layer structure, belongs to a rhombohedral system, and is characterized by being the single phase which the length of C axis which belonged as a hexagonal system is 14.15 Å or more, and a nickel atom, a cobalt atom, and manganese atoms are distributing uniformly with an atom level.

[0005]A lithium nickel cobalt manganese multiple oxide concerning this invention shows a charge-and-discharge curve which is high capacity very much and is characterized by 4V class flat and low polarization.

[0006]This invention provides a manufacturing method of a lithium nickel cobalt manganese multiple oxide in which said explained characteristic is shown. That is, a manufacturing method of positive active material for nonaqueous electrolyte secondary batteries of this invention comprises the following:

They are the bottom of existence of a complexing agent, and nickel in solution of pH 9-13. Cobalt.

Under an inert gas atmosphere, an atomic ratio with manganese reacts, and acts to an alkali solution as Mr. [of the mixed water solution of nickel salt, cobalt salt, and manganese salt which are 1:1:1 substantially / coprecipitation], and it is nickel.

Cobalt and the process 1 from which an atomic ratio with manganese obtains nickel cobalt manganese compound hydroxide and/or a nickel cobalt manganese multiple oxide which are 1:1:1 substantially, The process 2 of calcinating a mixture of said hydroxide and/or an oxide, and a lithium compound above 700 ** so that an atomic ratio of the sum total of nickel, cobalt, and manganese and an atomic ratio of lithium may be substantially set to 1:1.

[0007]Furthermore, a rechargeable lithium-ion battery containing a lithium nickel cobalt manganese multiple oxide concerning said this invention as a positive-electrode-active-material ingredient is contained in this invention. This cell has a charging and discharging characteristic which is high capacity and is characterized by 4V class very flat and low polarization rather than before. Hereafter, it is based on an embodiment of the invention, and this invention is explained in detail.

[0008]

[Embodiment of the Invention]The manufacturing method of the lithium manganese nickel multiple oxide concerning manufacturing method this invention consists of the following two processes.

(Process 1) In order that the atomic ratio of manufacture nickel of a raw material, cobalt, and manganese may obtain the raw material which is nickel cobalt manganese compound hydroxide and/or the nickel cobalt manganese multiple oxide which are 1:1:1 substantially, In the solution of pH 9-13, under existence of a complexing agent, the atomic ratio of nickel, cobalt, and manganese reacts and acts to an alkali solution as Mr. [of the mixed water solution of nickel salt, cobalt salt, and manganese salt which are 1:1:1 substantially / coprecipitation] The particles which the atomic ratio of nickel, cobalt, and manganese distributed uniformly with the atom level substantially by this coprecipitation Mr. method 1:1:1 can be obtained.

[0009]Restriction in particular does not have formation of a complexing agent and a complex of the nickel ion which generates usable nickel salt in solution here what is necessary be just possible. Specifically, nickel sulfate, nickel nitrate, and nickel chloride are mentioned. Similarly restriction in particular does not have formation of a complexing agent and a complex of the cobalt ion which generates usable cobalt salt in solution what is necessary be just possible. Specifically, cobalt sulfate, a cobalt nitrate, and a cobalt chloride are mentioned. The manganese ion which usable manganese salt does not have restriction in particular, and is generated in solution just forms a complexing agent and a complex. Specifically, manganese sulfate, manganese nitrate, and a manganese chloride are mentioned. It is contained if the range of the atomic ratio of nickel, cobalt, and manganese is about plus-or-minus 10% in 1:1:1 substantially in this invention, respectively. This value can be correctly measured by the various metal analysis methods (for example, the ICP method).

[0010]The pH value of solution has pH nine to 13 preferred range, and if it is necessity during a reaction, it is maintainable in this range by adding alkali metal hydroxide (for example, sodium hydroxide, a potassium hydrate). The complexing agent can form manganese ion and nickel ion, and a complex in solution, For example, an ammonium ion supply body, hydrazine (ammonium sulfate, ammonium chloride, ammonium carbonate, ammonium fluoride, etc.), ethylenediaminetetraacetic acid, nit lithograph triacetic acid, uracil 2 acetic acid, and a glycine

are mentioned. It is preferred to carry out under the atmosphere of inactive gas like nitrogen gas.

[0011](Process 2) The calcination by the baking process 2 so that the atomic ratio of the sum total of nickel of the raw material obtained at the process 1 and said raw material, cobalt, and manganese and the atomic ratio of lithium may be substantially set to 1:1, Preferably, it is 950–1000 ** still more preferably, and calcination—among air air current heating of at least 700–1000 ** of the mixtures [900–1000 ** of] obtained by mixing with a lithium compound is carried out.

[0012]Although there is no restriction in particular as an usable lithium compound, lithium hydroxide, lithium carbonate, a lithium nitrate, and lithium oxide are mentioned, for example. The mole ratio of a nickel cobalt manganese multiple oxide and a lithium compound is 1:1 substantially. If said mole ratio is a range about plus-or-minus 10% (preferably 3%) in 1:1 substantially, respectively, it is contained here. These values can be correctly measured by the various metal analysis methods (for example, the ICP method). Before calcinating, it is preferred to mix these enough.

[0013]The baking apparatus used for composition of the usual LiMn_2O_4 or LiNiO_2 can use it for calcination preferably. The usual atmospheric air of the atmosphere in the case of calcination is preferred.

[0014]The scanning type electron microscope (henceforth SEM) photograph of nickel cobalt manganese compound hydroxide which is a raw material obtained by the manufacturing method process 1 of nickel cobalt manganese compound hydroxide this invention is shown in drawing 1. The magnification of a photograph is 5000. A photograph shows that raw material particles are substantially spherical. It turns out that it fills up with primary particles densely. An example of the ultimate analysis value of a multiple oxide and other property values is shown in Table 1.

[0015]

Table 1 set ** nickel(wt%) 21.1 Co (wt%). 21.1 Mn(wt%) 19.8 nickel (mol%). 33.4 Co(mol%) 33.2 Mn (mol%). 33.4 tap-density (g/cc) 1.95 bulk density (g/cc) — 1.23 particle diameter (micrometer) 9.0 — specific surface area (m^2/g) 13.5 SO_4 (%) 0.03 nickel:Co:Mn 1.00:1.00:1.00[0016]The result

of having observed the shape of the lithium nickel cobalt manganese multiple oxide obtained by the manufacturing method of lithium nickel cobalt manganese multiple oxide this invention by SEM is shown in drawing 2. The magnification of a photograph is 5000. The X diffraction figure of the lithium nickel cobalt manganese multiple oxide ghost concerning this invention is shown in drawing 3. Drawing 3 shows that the lithium nickel cobalt manganese multiple oxide obtained by the manufacturing method of this invention is the layer structure which has high crystallinity.

[0017]The rechargeable lithium-ion battery of rechargeable lithium-ion battery this invention is a rechargeable lithium-ion battery containing said lithium nickel cobalt manganese multiple oxide as a positive-electrode-active-material ingredient. Since the lithium nickel cobalt manganese multiple oxide concerning this invention is contained as a positive-electrode-active-material ingredient, this cell has a charging and discharging characteristic characterized by very flat and low polarization in the 4V neighborhood, as shown in drawing 4. The capacity is about 200 mAh/g and is very high.

[0018]

[Example]13L Water to the cylindrical shape reaction vessel of 15L provided with example 1 agitator and the overflow pipe After putting in, Having added the sodium hydroxide solution 30%, having carried out bubbling of the nitrogen gas by the flow for 0.5L/into the reaction vessel, and removing dissolved oxygen until pH was set to 10.9, temperature was held at 50 ** and it stirred with constant speed. Next, the mixed liquor of the 1.7 mol/L nickel sulfate aqueous solution and 1.5 mol/L cobalt sulfate solution which were mixed so that the atomic ratio of nickel:Co:Mn might be set to 1:1:1, and 1.1 mol/L manganese sulfate solution is received in 6 mol/L ammonium sulfate solution at mixed water solution capacity. 5% (v/v), in addition, 4wt% hydrazine solution was added to the reaction vessel by 10-cc the flow for /to the amount of mixed water solutions 1.3% (v/v) in order to remove the dissolved oxygen in this mixed solution further. Sodium hydroxide was added intermittently 30% and nickel cobalt manganese compound hydroxide particles were made to form so that the solution in a reaction vessel may furthermore be set to

pH 10.9.

[0019]After the inside of a reaction vessel was in the stationary state, nickel cobalt manganese compound hydroxide particles were continuously extracted from the overflow pipe, and after rinsing, it filtered, and dried at 100 °C for 15 hours, and nickel cobalt manganese compound hydroxide which it is in the end of dried powder was obtained.

[0020]Next, so that an atomic ratio may be set to $\text{Li}/(\text{nickel}+\text{Co}+\text{Mn})=1.0$ to $(\text{nickel}+\text{Co}+\text{Mn})$ of the obtained manganese nickel compound hydroxide, Weighing of the lithium hydroxide monohydrate was carried out, and it fully mixed with nickel cobalt manganese compound hydroxide, and in atmospheric air, after 15-hour calcination, it ground and the lithium nickel cobalt manganese multiple oxide was obtained at 1000 °C.

[0021]The electrochemical characteristics of said obtained lithium nickel cobalt manganese multiple oxide were evaluated by creating a coin type cell. In the positive electrode material, polyvinylidene fluoride resin (PVDF) which is acetylene black and the binder which are said obtained lithium nickel cobalt manganese multiple oxide and a conducting agent was mixed at a rate of 88:6:6 by the weight ratio, and the sheet-shaped molded product was obtained to it. And pierced this molded product disc-like, it was made to dry at the temperature of 80 °C in a vacuum for about 15 hours, and the anode was obtained. The lithium metal fabricated by the sheet shaped was pierced disc-like, and it was considered as the negative electrode. the ratio by which the electrolysis solution added LiPF_6 [1-mol] to the mixed solvent of ethylene carbonate (EC):diethyl carbonate (DEC) =1:1 (volume ratio) using the fine porous membrane of polyethylene as a separator -- water electrolysis liquid was used. Charge and discharge were repeated for this cell for an examination between 2.5-4.7V by the constant current of ten hour rates. The charge-and-discharge curve at this time was shown in drawing 4.

[0022]The charge-and-discharge capacity of about 200 mAh/g could be obtained the first stage, and it turned out that discharge voltage is also 4V class. The electrochemical characteristics which have little degradation and in which the capacity drop accompanying a cycle also has it were shown. [still better]

[0023]

[Effect of the Invention]With the manufacturing method concerning this invention, have the layer structure of high crystallinity and it belongs to a rhombohedral system, The length of C axis which belonged as a hexagonal system is a lithium nickel cobalt manganese multiple oxide which is 14.15 Å or more, the atomic ratio of nickel, cobalt, and manganese is 1:1:1 substantially, and each atom is the single phase uniformly distributed with the atom level. still bigger capacity -- and the positive active material for nonaqueous electrolyte batteries by which the charging and discharging characteristic of high surface smoothness and low polarization nature being shown can be obtained. The outstanding rechargeable lithium-ion battery containing this lithium nickel cobalt manganese multiple oxide as a positive-electrode-active-material ingredient can be obtained.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]It is a SEM photograph of the lithium nickel cobalt manganese compound hydroxide produced in this invention.

[Drawing 2]It is a SEM photograph of the lithium nickel cobalt manganese multiple oxide produced in this invention.

[Drawing 3]It is an X diffraction figure of the lithium nickel cobalt manganese multiple oxide produced in this invention.

[Drawing 4]It is a figure showing the charge-and-discharge curve of the coin type cell which used as positive active material the lithium nickel cobalt manganese multiple oxide produced in this invention.

[Translation done.]

【物件名】

刊行物 3

【添付書類】

刊行物 3

6  028

(19) 日本国特許庁 (JP)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開2003-59490

(P2003-59490A)

(43) 公開日 平成15年2月28日 (2003.2.28)

(51) Int.Cl.⁷

識別記号

FI

フィート (参考)

H01M 4/58
10/40H01M 4/58
10/405H029
Z 5H050

審査請求 未請求 請求項の数 6 OL (全 6 頁)

(21) 出願番号 特願2001-247816(P2001-247816)

(22) 出願日 平成13年8月17日 (2001.8.17)

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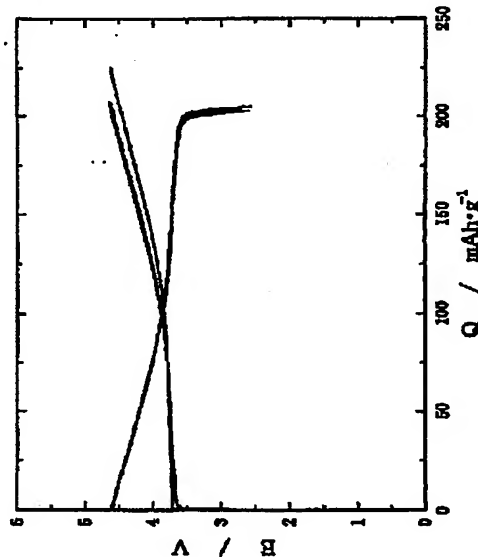
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(54) 【発明の名称】 非水電解質二次電池用正極活性物質及びその製造方法

(57) 【要約】

【課題】 優れた特性を有する、リチウムイオン二次電池用正極活性物質として有用なリチウムニッケルコバルトマンガン複合酸化物およびその製造方法、さらにはそれを用いたリチウムイオン二次電池を提供する。

【解決手段】 本発明にかかるリチウムニッケルコバルトマンガン複合酸化物は、ニッケルとコバルトとマンガンの原子比が実質的に1:1:1である、 $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ なる組成式で表されるものであり、高結晶性の層状構造を有し、菱面体晶系に属し、六方晶系として帰属したC軸の長さが14.15オングストローム以上であることを特徴とする。



(2)

特開2003-59490

【特許請求の範囲】

【請求項1】 実質的に同比率のニッケル元素、コバルト元素、及びマンガン元素を含む高結晶性の酸化物の結晶粒子からなる非水電解質二次電池用正極活物質。

【請求項2】 前記酸化物がリチウム元素を含有することを特徴とする請求項1に記載の非水電解質二次電池用正極活物質。

【請求項3】 ニッケル元素、コバルト元素、及びマンガン元素の比率の誤差が10原子%以内であることを特徴とする請求項1又は2のいずれかに記載の非水電解質二次電池用正極活物質。

【請求項4】 前記酸化物に含まれるリチウム元素、ニッケル元素、コバルト元素、及びマンガン元素が、 $0.97 \leq Li/(Ni+Co+Mn) \leq 1.03$ を満たすことを特徴とする請求項1～3のいずれかに記載の非水電解質二次電池用正極活物質。

【請求項5】 pH9～13の水溶液中で錯化剤の存在下、ニッケルとコバルトとマンガンとの原子比が実質的に1:1:1であるニッケル塩とコバルト塩とマンガン塩との混合水溶液を不活性ガス雰囲気下でアルカリ溶液と反応、共沈殿させてニッケルとコバルトとマンガンの原子比が実質的に1:1:1であるニッケルコバルトマンガン複合酸化物および/またはニッケルコバルトマンガン複合酸化物を得る工程1と、ニッケルとコバルトとマンガンの合計の原子比とリチウムの原子比が実質的に1:1:1となるように、前記水酸化物および/または酸化物とリチウム化合物との混合物を700℃以上で焼成する工程2とからなることを特徴とする、請求項1～4のいずれかに記載のリチウムニッケルコバルトマンガン複合酸化物の製造方法。

【請求項6】 請求項1～4のいずれかに記載のリチウムニッケルコバルトマンガン複合酸化物を正極活性物質成分として含有することを特徴とする、リチウムイオン二次電池。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、優れた特性を有する、リチウムイオン二次電池用正極活物質として有用なリチウムニッケルコバルトマンガン複合酸化物およびその製造方法、さらにはそれを用いたリチウムイオン二次電池に関する。

【0002】

【従来の技術】 近年、コードレス、ポータブルなAV機器およびパソコンなどの普及に伴い、それらの駆動用電源である電池についても、小型、軽量および高エネルギー密度の電池への要望が強まっている。特にリチウム二次電池は、高エネルギー密度を有する電池であることから、次世代の主力電池として期待されている。現在市販されているリチウム二次電池の大半は正極活物質として4Vの高電圧を有する $LiCoO_2$ が用いられている

が、Coが高価であることからその価格が高い。このことから安価でかつ $LiCoO_2$ の優れた性能を損なわず又はより優れた性能を有するものが要求されている。

【0003】

【課題を解決するための手段】 本発明者はかかる要望を満たす $LiCoO_2$ に代わる物質を探索すべく鋭意研究し、以下に説明する製造方法を用いることにより、4V級正極活物質としてニッケル、コバルトおよびマンガンの原子比が実質的に1:1:1である $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ なる組成を有するものが、リチウムイオン二次電池に適用するに望まれる種々の優れた特性を有することを見出した。さらには、この本発明にかかるリチウムマンガンニッケル複合酸化物を用いた優れた特性を有するリチウムイオン二次電池を得られることを見出し本発明を完成するに至った。

【0004】 すなわち、本発明にかかる非水電解質二次電池用正極活物質は、実質的に同比率のニッケル元素、コバルト元素、及びマンガン元素を含む高結晶性の構造を有する酸化物の結晶粒子からなる非水電解質二次電池用正極活物質である。また、本発明にかかる非水電解質二次電池用正極活物質は、前記酸化物がリチウム元素を含有することを特徴とする。また、本発明にかかる非水電解質二次電池用正極活物質は、ニッケル元素、コバルト元素、及びマンガン元素の比率の誤差が10原子%以内であることを特徴とする。さらに、本発明にかかる非水電解質二次電池用正極活物質は、前記酸化物に含まれるリチウム元素、ニッケル元素、コバルト元素、及びマンガン元素が、 $0.97 \leq Li/(Ni+Co+Mn) \leq 1.03$ を満たすことを特徴とする。ここで、本発明にかかる非水電解質二次電池用正極活物質の結晶構造的特徴として、層状構造を有し、菱面体晶系に属し、六方晶系として帰属したC軸の長さが14.15オングストローム以上でかつニッケル原子とコバルト原子とマンガン原子が原子レベルで均一に分散している単一相であることを特徴とする。

【0005】 さらに、本発明にかかるリチウムニッケルコバルトマンガン複合酸化物は極めて高容量でありかつ4V級の平坦で低い分極を特徴とする充放電曲線を示す。

【0006】 また、本発明は、前記説明した特性を示すリチウムニッケルコバルトマンガン複合酸化物の製造方法を提供するものである。すなわち、本発明にかかる非水電解質二次電池用正極活物質の製造方法は、pH9～13の水溶液中で錯化剤の存在下、ニッケルと、コバルトと、マンガンの原子比が実質的に1:1:1であるニッケル塩とコバルト塩とマンガン塩との混合水溶液を不活性ガス雰囲気下でアルカリ溶液と反応、共沈殿させてニッケルと、コバルトと、マンガンの原子比が実質的に1:1:1であるニッケルコバルトマンガン複合酸化物および/またはニッケルコバルトマンガン複合酸

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化物を得る工程1と、ニッケルとコバルトとマンガンとの合計の原子比とリチウムの原子比が実質的に1:1となるように、前記水酸化物および/または酸化物とリチウム化合物との混合物を700℃以上で焼成する工程2とからなることを特徴とする。

【0007】さらに本発明には、前記本発明にかかるリチウムニッケルコバルトマンガン複合酸化物を正極活性物質成分として含有することを特徴とする、リチウムイオン二次電池が含まれる。かかる電池は、従来よりも高容量でありかつ4V級の極めて平坦でかつ低い分極を特徴とする充放電特性を有する。以下、本発明を、発明の実施の形態に即して詳細に説明する。

【0008】

【発明の実施の形態】 製造方法

本発明に係るリチウムマンガンニッケル複合酸化物の製造方法は、次の2つの工程からなることを特徴とする。

(工程1) 原料の製造

ニッケル、コバルト、マンガンの原子比が実質的に1:1:1であるニッケルコバルトマンガン複合水酸化物および/またはニッケルコバルトマンガン複合酸化物である原料を得るため、pH9~13の水溶液中で錯化剤の存在下、ニッケルとコバルトとマンガンの原子比が実質的に1:1:1であるニッケル塩、コバルト塩、マンガン塩の混合水溶液をアルカリ溶液と反応、共沈殿させることを特徴とする。かかる共沈殿法によりニッケルとコバルトとマンガンの原子比が実質的に1:1:1で原子レベルで均一に分散した粒子を得ることができる。

【0009】ここで使用可能なニッケル塩は、水溶液中で生成するニッケルイオンが錯化剤と錯体を形成可能なものであればよく特に制限はない。具体的には硫酸ニッケル、硝酸ニッケル、塩化ニッケルが挙げられる。同様に使用可能なコバルト塩は、水溶液中で生成するコバルトイオンが錯化剤と錯体を形成可能なものであればよく特に制限はない。具体的には硫酸コバルト、硝酸コバルト、塩化コバルトが挙げられる。使用可能なマンガン塩は特に制限はなく水溶液中で生成するマンガンイオンが錯化剤と錯体を形成可能なものであればよい。具体的には硫酸マンガン、硝酸マンガン、塩化マンガンが挙げられる。本発明においてニッケル、コバルト、マンガンの原子比が実質的に1:1:1とは、それぞれプラスマイナス10%程度の範囲であれば含まれる。またこの値は種々の金属分析方法（例えばICP法）により正確に測

定することができる。

【0010】水溶液のpH値は、pH9~13の範囲が好ましく、反応中必要ならばアルカリ金属水酸化物（例えば水酸化ナトリウム、水酸化カリウム）を添加することによりこの範囲に維持することができる。また、錯化剤は、水溶液中でマンガンイオンおよびニッケルイオンと錯体を形成可能なものであり、例えばアンモニウムイオン供給体（硫酸アンモニウム、塩化アンモニウム、炭酸アンモニウム、弗化アンモニウム等）、ヒドラジン、エチレンジアミン四酢酸、ニトリト三酢酸、ウラシル二酢酸、グリシンが挙げられる。また窒素ガスのような不活性ガスの雰囲気で行うことが好ましい。

【0011】(工程2) 焼成

工程2での焼成は、工程1で得られた原料と、前記原料のニッケル、コバルト、マンガンの合計の原子比とリチウムの原子比が実質的に1:1となるように、リチウム化合物と混合し、得られる混合物を少なくとも700~1000℃、好ましくは900~1000℃、更に好ましくは950~1000℃で、空気気流中焼成加熱するものである。

【0012】使用可能なリチウム化合物としては特に制限はないが、例えば水酸化リチウム、炭酸リチウム、硝酸リチウム、酸化リチウムが挙げられる。ニッケルコバルトマンガン複合酸化物とリチウム化合物とのモル比は、実質的に1:1である。ここで前記モル比が実質的に1:1とは、それぞれプラスマイナス10%（好ましくは3%）程度の範囲であれば含まれる。またこれらの値は種々の金属分析方法（例えばICP法）により正確に測定することができる。焼成する前にこれらを十分混合しておくことが好ましい。

【0013】焼成には、通常の $LiMn_2O_4$ や $LiNiO_2$ の合成に用いられる焼成装置が好ましく使用できる。焼成の際の雰囲気は通常の大気雰囲気が好ましい。

【0014】ニッケルコバルトマンガン複合水酸化物 本発明の製造方法工程1により得られる原料であるニッケルコバルトマンガン複合水酸化物の走査式電子顕微鏡（以下SEMという。）写真を図1に示す。写真の倍率は5000倍である。写真から原料粒子は実質的に球状であることがわかる。また、1次粒子が密に充填されていることがわかる。複合酸化物の元素分析値およびその他の物性値の一例を表1に示す。

【0015】

表 1

組 成

Ni (wt%)	21.1
Co (wt%)	21.1
Mn (wt%)	19.8
Ni (mol%)	33.4
Co (mol%)	33.2
Mn (mol%)	33.4

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Ni : Co : Mn 1.00 : 1.00 : 1.00

【図1】本発明において作製したリチウムニッケルコバルトマンガン複合水酸化物のSEM写真である。

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【図2】本発明において作製したリチウムニッケルコバルトマンガン複合酸化物のSEM写真である。

【図3】本発明において作製したリチウムニッケルコバルトマンガン複合酸化物のX線回折図である。

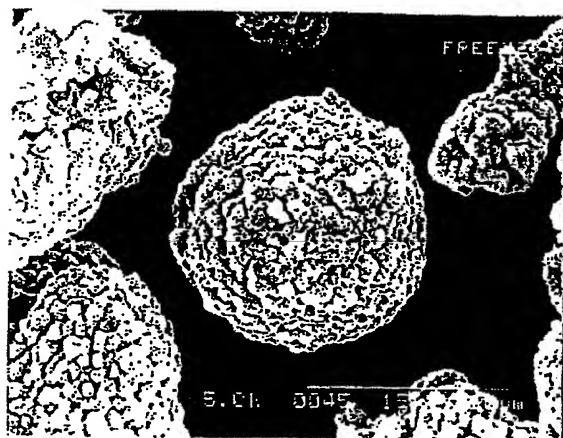
【図4】本発明において作製したリチウムニッケルコバルトマンガン複合酸化物を正極活物質としたコイン型電池の充放電曲線を示す図である。

【図1】



Ni-Co-Mn複合水酸化物
(Ni:Co:Mn=1:1:1)

【図2】

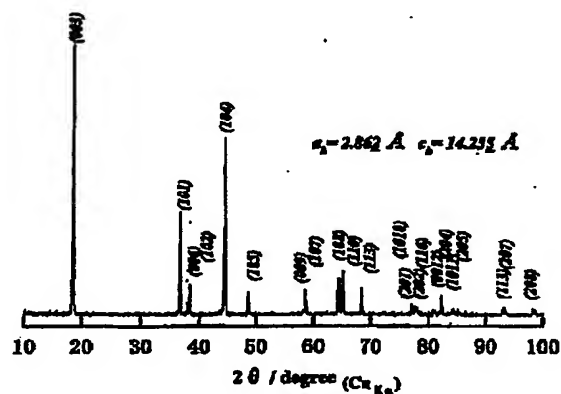


$\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$

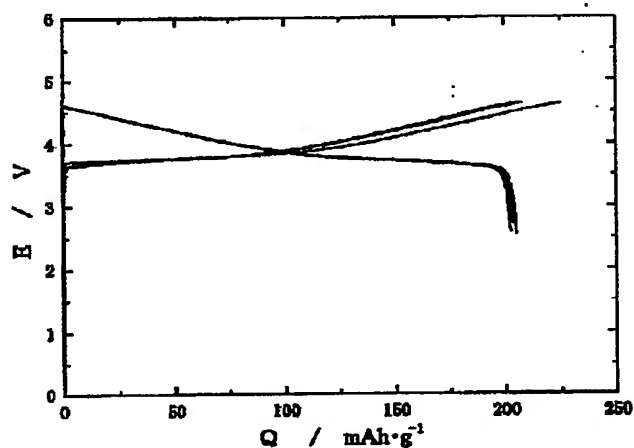
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【図3】



【図4】



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Fターム(参考) 5H029 AJ00 AJ14 AK03 AL12 AM03
 AM05 AM07 CJ02 CJ08 HJ02
 5H050 AA00 AA19 BA16 BA17 CA08
 CA09 CB12 GA02 GA10 GA12
 HA02 HA14